MULTISCALE MODELLING OF POLYMER PROPERTIES

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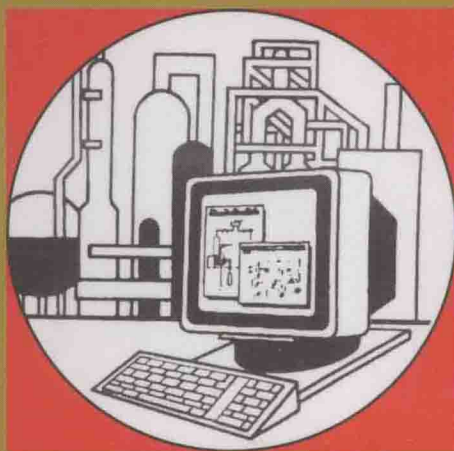
COMPUTER-AIDED CHEMICAL ENGINEERING

Advisory Editor: R. Gani

Preface

This book is a direct result of project PMILS (**P**olymer **M**olecular Modelling at **I**ntegrated **L**ength/time **S**cales) – a European project funded by the European Commission's 5th Framework Programme. The PMILS project addressed the fundamental question of predicting macroscopic properties of polymeric materials from their molecular constitution and processing history. It combines a wide range of modelling tools (quantum mechanical, molecular modelling, mesoscopic, macroscopic) and experimental methods.

Project PMILS was a pioneering project in the area of Industrial Technologies - Materials. In PMILS a multidisciplinary team of highly qualified partners from Belgium, Denmark, France, Greece, Norway, United Kingdom and Spain contributed expert know-how on areas which at first sight might seem unrelated (quantum chemistry, molecular modelling, polymer synthesis, viscoelasticity, process optimization, etc.) but which could be brought to bear on multiscale, hierarchical modelling of polymers in a complementary fashion. The project was co-ordinated by the Universidad Politécnica de Madrid (UPM). It is the UPM's principal investigator (Prof. M. Laso) together with Dr. Eric Perpète, of the Laboratoire de Chimie Théorique Appliquée at F.U.N.D.P. Namur, who have undertaken the editorial work of the present volume in the "Computers Aided Chemical Engineering" series.

It had been a challenge to bring the team together on a European level, because people coming from different modelling backgrounds had to understand each others 'modelling language' and had to find out which parameters were needed as input for the other partners. The team used a systematic hierarchical approach for the organisation of these diverse methods and applied the tools for the understanding of the macroscopic properties. It became clear that these modelling tools are very versatile and could be adapted to a multitude of problems.

The support given to PMILS clearly demonstrates the relevance the EC gives to advanced combined approaches to complex problems in Materials Science. Furthermore, in the spirit of continued support of European Research, the 6th Framework Programme the NMP priority (Nanotechnologies, Materials and Production) subsequently opened a call in the area of "Modelling and design of Multifunctional Materials". The objective was to use the powerful tools of materials modelling for the understanding of the complex behaviour of new knowledge-based materials and their industrial use. As a result of this call, projects are now funded in a variety of areas (e. g. design of polymers of controlled permeability, thin films for energy storage, corrosion of coatings, modelling of noise and vibration) which showcase the Commission's committment to the development of acvanced multi-scale simulation methods.

Furthermore, a coordinated call with the National Science Foundation of the United States on Computational Materials Science was also organised to fund joint project proposals which address properties and phenomena that span multiple time and length scales and require multiscale modelling involving a balanced participation of partners from EU and US. It is thus very satisfactory to see that promising lines of research initiated in PMILS have resulted in successful proposals to this EC-NSF coordinated call. Materials research is very much alive in Europe.

The work programme for Materials Sciences in the 7th Framework Programme is being prepared as this book goes to press. The contents of this book may inspire and motivate readers to create new ways of applying modelling for the improvement of Materials Science and for meeting the needs of European Industry.

Dr. Astrid-Christina Koch
European Commission
Directorate General for Research
Industrial Technologies – Materials

Brussels, May 2006

Introduction

Polymeric materials constitute a very widespread and economically important family of materials. It is no exaggeration to say that they are ubiquitous in our daily lives. Yet, in spite of their very widespread use, a good deal of their physical and chemical behaviour and not a little of the phenomena underlying their production technology is still far from being understood.

While the basic concept of a polymer goes back to the 1920s and very great advances have continuously been made since, some of the most fundamental questions regarding their properties and performance remain unanswered. It is not difficult to select a few prominent factors responsible for this unsatisfactory but also challenging state of affairs:

- Unlike low-molecular-weight substances, bulk amounts of polymers invariably contain molecules of widely different molecular size: they are polydisperse and this polydispersity is has a major impact on most macroscopic static and, above all, dynamic properties.

- Even in the ideal monodisperse case, the dynamic processes that take place in polymers at the molecular level involve not just one or a few characteristic time and length scales, but a whole hierarchy, ranging from the very fast, very small scales (e.g. single-bond vibration) to the slow and large ones (e.g., whole-polymer-chain relaxation). Characteristic spatial and temporal scales can easily span 10 orders of magnitude.

- Only exceptionally do polymers form well-developed crystalline solids. In addition, the existence or even prevalence of amorphous domains is almost universal in the solid state.

- Polymers lend themselves ideally to the formation of "hybrid" molecules or copolymers, the properties of which frequently depend in a very complex fashion on the nature, proportions and sequence of the intervening monomers.

Depending on the specific case, i.e., on which property of which polymer and for which application, efforts to understand and predict the effect of these factors, (plus several others we have omitted) on final material properties and general dynamic behaviour face barriers which are more often than not unsurmountable.

On the other hand, it is precisely this complexity that makes polymers "tailorable" materials *par excellence*; hence the great interest and relevance of methods of prediction of polymer properties and behaviour in the most general sense.

Although widely differing in their subject matter and in their methodological approaches, the contributions collected in this multi-author book share a common unifying theme: the combined use of two or more techniques and the communication between description levels which reside at very different spatial or temporal characteristic scales. The authors are of course not alone in this effort: "multiscale", "hierarchical", "multilevel" are words that, over the last decade, have attained considerable visibility. They turn up in the most cursory search as buzzwords in almost any conceivable field of materials science but also in physics.

A little historical reflection shows that "multiscale" views of materials have existed for a long time. What are well-established fields like statistical mechanics, continuum mechanics, electronics, plasticity theory, etc if not the ultimate two-level approach: one in which the atomistic and electronic reality, with its unimaginably large number of microscopic degrees of freedom, gets condensed down to a few equations and numerical values of parameters. In this admittedly narrow sense, multilevel is not that new.

There is however more to these terms than meets the eye: while Materials Science long ago adapted and developed tools to perform the atomistic-continuum jump, the driving force was the blatant *impossibility* of handling the myriad of atomistic/electronic details lurking behind the single number that quantifies a macroscopic property. In many cases, there was also no *necessity* to do so, since phenomenology complemented by good experiments was sufficient to cover most design needs.

What then is new about present-day "multiscale" methods? At a very obvious level, the drive to be able to condense and carry the information made available by powerful computers at the smallest scales all the way to the macroscopic level, where its usefulness is presumably greatest. At a deeper level, and this is

especially meant for dynamic properties and behaviour away from equilibrium, we dare to say that the reason for crossing scale barriers by coarse-graining the more-detailed description level is the *undesirability* to simulate reality in its full detail. Carrying out a large-scale molecular-dynamics simulation of say, 10^{12} atoms up to the macroscopic observation time of one second may be feasible in the not-too-distant future. Such brute-force simulations can be considered as computer experiments that can closely mimic the problem at hand. Computer experiments require few assumptions and not much in the way of insight, which may be considered as an asset or as a liability. It is our personal opinion, and we hope this book proves it to a certain extent, that the most promising path for far reaching advances in modelling polymeric materials is that of understanding through simplicity, that is, looking for the coarsest possible description of phenomena of interest while avoiding oversimplification. It is in this sense that our statement about the *undesirability* to simulate reality in its full detail should be understood.

In some chapters of this book the reader will find examples of maximal scale jumping: for example, going directly from the electronic structure of a given compound to something as macroscopic as the value of a parameter in an equation of state. Although the two areas involved in this work, quantum chemical methods and equations of state (EOS) in classical equilibrium thermodynamics, apparently are totally unrelated, a judicious and intuitively appealing coarse-graining makes it possible to predict numerical values for constants appearing in the EOS which have been hitherto almost invariably obtained by regression.

Other sections will introduce mesoscopic descriptions of polymers and link them either to the atomistic level or to the macroscopic level or even to both. In these cases, the goal is to be able to predict not only static thermodynamic properties but also to do so for transport properties (diffusivity, viscosity, etc) and even to use these directly in complex flow calculations. Again, straightforward coarse-graining rules are applied, mostly based on intuition or on the well established basis of linear response theory.

It is however essential to emphasize in this preface that, complex though the calculation/simulation work at a single description level may be, the major and frequently unrecognized challenge facing multiscale or coarse-graining efforts lies elsewhere: in the need to guarantee the thermodynamic consistency of the simplification process. While intuition is a valid and often reliable tool, the danger of leaning too heavily on what seem natural ways of extracting and passing information to higher hierarchical levels of description should not be

underestimated. Fortunately, recent developments in the area of non-equilibrium thermodynamics, that go beyond linear response theory, furnish a reliable guide to consistency. If a prediction can be risked at this stage, it is the well-nigh certainty that we will witness a healthy growth in thermodynamically guided simulations and coarse-graining. Einstein's, perhaps apocryphal, words are especially fitting: "Everything should be made as simple as possible, but not simpler".

Although the subject of this book is integration, as a matter of presentation the material it contains must be divided. We have chosen to divide the book into two sections: the first contains chapters focusing on methodological aspects while chapters in the second section are concerned with the study of practical cases. The chapters in each section are arranged in ascending order according to the scale at which the individual studies are primarily addressed, e.g., from quantum or atomistic scales to the macroscopic.

We would like to express our sincere gratitude to all the authors for their excellent contributions, to Dr. V. Wathelet for her efficient help in assembling this volume, as well as to Dr. J.-L. Vallés and Dr. A.-C. Koch who continuously supported our project, and consequently share its success.

Madrid and Namur, May 2006   M. Laso, E.A. Perpète

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Part I : Methodological Aspects

Chapter 1

Calculation of Hartree-Fock Energy Derivatives in Polymers

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1. Introduction

1.1. General framework

Hermann Staudinger, the precursor of polymer's chemistry, received the 1953 Nobel Prize for his discoveries in macromolecular chemistry. Today, these compounds have invaded numerous fields like medicine, informatics, aeronautics, ... such that world production (in volume) of polymers is now larger than that of steel. This success originates from the ability of designing macromolecules with very diverse properties. Indeed, the mechanical, optical and electrical properties of polymers can easily be tuned by chemical transformation. New polymers with high performance in electro-optic, micro-electronic and nonlinear optics are intensively looked for. In this framework of multidisciplinary research, theoretical chemistry can be viewed as an initial and often essential step. Indeed, it allows the evaluation of material properties, as well as the design of structure-property relationships, so that the synthesis can be driven to the most promising structures. To satisfy such criteria, it is necessary to be able to accurately determine the structures and properties of polymers. For instance, the knowledge of the ground-state equilibrium geometry is often a necessary prerequisite to the calculation of other properties.

Many textbooks and recent reviews describe several aspects of quantum-mechanical calculations on polymers [1-4]. In the present contribution, we only summarize the results of our recent work aiming at the

accurate determination of Hartree-Fock (HF) energy derivatives in stereoregular polymers [5-17].

1.2. Oligomer versus polymer approach

Two methods can be considered for evaluating the properties of infinite periodic chains. In the oligomeric approach, one uses standard quantum chemistry packages to compute the desired properties on increasingly large chains and extrapolates to the infinite chain limit. For instance, one calculates the difference of polarizability between consecutive chains in the alkane series (methane, ethane, propane, butane, ...) and obtains, once sufficiently large compounds are used, a valuable approximation for the response of the infinitely long polyethylene. This is illustrated in Figure 1 for hydrogen fluoride chains. As can be seen, the saturation with respect to oligomer size can be very slow. In general, the more the investigated property is related to higher-order derivatives of the energy, the slower the saturation. Indeed, in Figure 1, the pentamer allows to determine the energy with a very small error (0.001 %) whereas the inaccuracy on the force is still larger than 5% [5]. Similar effects are obtained for hyperpolarizabilities: the higher the derivative order, the slower the saturation.
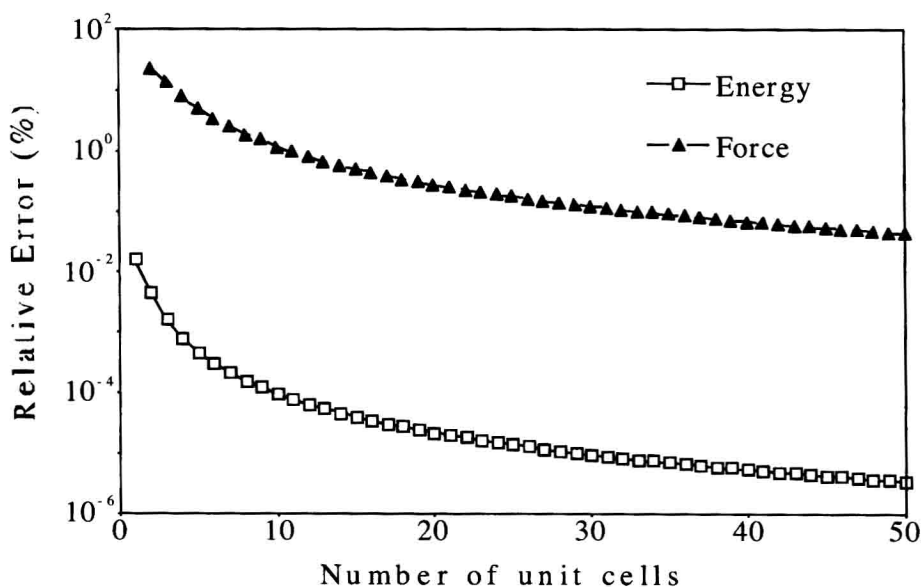

Figure 1: Evolution with oligomer size of the relative errors on the total energy and force for model fluorhydric acid chains. The polymer value is used as reference to determine the errors.